# Weed Science Society of America

# The Role of Chemical Research in Developing Selective Weed Control Practices[1]

## H. Gysin[2]

Shortly after 1934 when Kögl and co-workers found that indole–3–acetic acid

—CH$_2$COOH
N
H
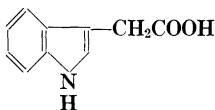
is a substance which has cell elongation activity in plants, many attempts were made to find other chemicals showing an indole–acetic–acid-like activity. It is 25 years now since Zimmermann and Wilcoxon found that naphthyl–1–acetic acid

CH$_2$COOH

and some other aryl–acetic acids are active plant regulating compounds also. With these experiments it could be shown that the indole–nucleus is not essential for a plant growth regulator. The findings of Irvine showed that 2–naphthoxy–acetic acid
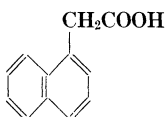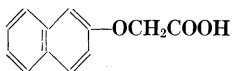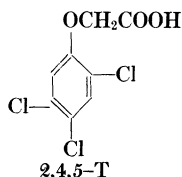
—OCH$_2$COOH

is equally active as a phytohormone. This indicates that the acetic acid has not necessarily to be linked to the naphthalene ring directly. The naphthoxy–acetic acid was further modified chemically and became the starting point for the most widely used phytohormones: 2,4–D, MCPA and 2,4,5–T.

OCH$_2$COOH
—Cl
Cl
2,4–D

OCH$_2$COOH
—CH$_3$
Cl
MCPA

OCH$_2$COOH
—Cl
Cl—
Cl
2,4,5–T
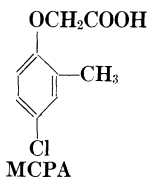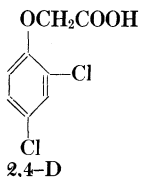
The history of the discovery and investigation of 2,4–D and MCPA never became completely clear to the outsider as the initial work was done during the war and was covered by secrecy regulations. From 1942 on various laboratories in the world made a concentrated effort

541

to find within this general group of chemicals more active or more selective compounds. This effort led to the discovery of quite a number of 2,4– or 2,4,5–substituted phenol derivatives with side-chains being acetic–, propionic–, or butyric acid. This proved to be a most fruitful line of investigation as a dozen or more products resulted from it and are on the market today. In addition to the alteration of the structure of the side-chain of 2,4–D, other ways were followed with the goal to change the activity of 2,4–D and the like. If the oxygen atom of phenoxy–acetic acids is replaced by an amino group or by a sulfur atom the respective 2,4–dichloro–phenyl-glycine

$$NHCH_2COOH$$
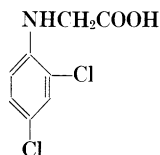
and the 2,4–dichloro–phenyl–thio–acetic acid

$$SCH_2COOH$$
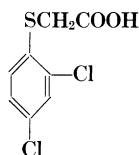
are still active growth regulators. As Wain gave a comprehensive study on the chemical structure in relation to the growth regulating properties of the 2,4–D–type chemicals in the second volume of "Advances in Pest Control Research", I may be permitted to make a few further remarks on this chapter only: Quite a number of factors are known today which seem to be responsible for the activity or inactivity of substituted phenol–, naphthol–, phenyl–, indole–fatty and the substituted benzoic acids. It seems, however, premature to use for the synthesis of new compounds in this field existing theories only and to synthesize only chemicals which fit the theoretical requirements. According to the still widely accepted two-point theory for example a 2,6–dichloro–phenoxy–acetic derivative should be inactive. It was found, however, that 2,6–dichloro–phenoxy–aceta-mide has a considerable activity. Another good example how biological effects may be changed by altering the structure is 2,4–DB:

$$OCH_2CH_2CH_2COOH$$
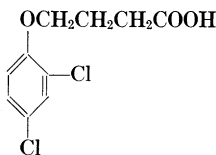
2,4–DB

It could be shown that this compound is much more selective than 2,4–D and various investigators especially Wain and his co-workers

could find the explanation of this increased selectivity. Some plants are able to transform 2,4–DB by $\beta$–oxidation into the active 2,4–D while others do not possess this oxidation system and, therefore, remain unaffected. It was very fortunate that many weeds are able to produce this conversion more effectively than the crops so that this phenomenon is applicable practically. Another attempt to mask the active principle and to leave it to secondary factors to transform the compound into an active chemical is sesone:

$$OCH_2CH_2OSO_3Na$$
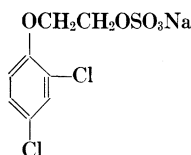


It is believed that this compound can be oxidised, being a derivative of 2,4–dichloro–phenoxy–ethanol, to 2,4–D. Sesone applied to the foliage of a plant is not active per se but is oxidised in the soil to 2,4–D. 2,4–Dichloro–phenoxy–ethyl–benzoate (2,4–DEB)

$$O–CH_2–CH_2O–C{=}O$$
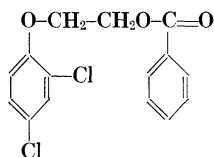


and tris–(2,4–dichlorophenoxy–ethyl) phosphite (2,4–DEP)
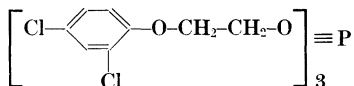


are based on the same principle. They are of low activity when applied on the foliage but are converted in the soil to the active herbicide. Their conversion time is dependent on the soil moisture and temperature as is their residual effect. In addition to the phenoxy–fatty acid derivatives the carbamate herbicides are another field where the relationship between chemical structure and herbicidal activity was studied. As early as 1929 phenyl urethane was known as a germination inhibitor. It was, however, only due to Templeman and Sexton that 15 years ago a comprehensive study was made on a number of aryl–carbamic esters. While on the one hand the replacement of the ethyl alcohol in phenylurethane by isopropyl alcohol led to a considerable increase of activity, the introduction of a chlorine atom into the phenyl-ring, especially in 3–position doubled or tripled the activity. The introduction of a chlorine atom into IPC-yielding chloro–IPC (CIPC)—increases the resistance of this latter compound to a microbial breakdown in the soil and prolongs its residual effectiveness:
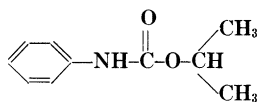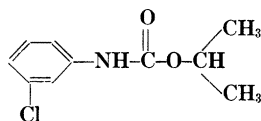
IPC                    CIPC (much more active than IPC)

Shaw published in 1953 a study on the activity of some 45 carbamates and could show that secondary butanol used instead of isopropanol in CIPC led to a slightly more active carbamate:



CIPC                    slightly more active than CIPC

If the same change is made in IPC a much more active compound is obtained in the secondary butyl analogue:



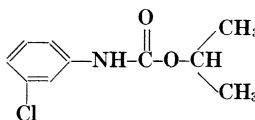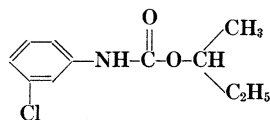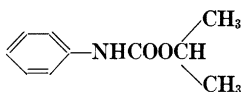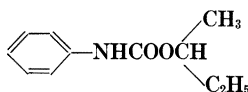IPC                    much more active than IPC

In addition to the chlorine atom in the 3–position of the phenyl ring a methyl group in the same position does not alter fundamentally the activity of CIPC:
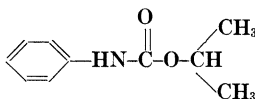


|  |  |
|---|---|
| 3–$CH_3$ | highly active |
| 3–$NO_2$ | moderately active |
| 3–OH | trace of activity |

highly active

But substituents such as the nitro– and especially the hydroxy–group lead to a considerable or total loss of the herbicidal activity. The introduction of different substituents into various positions of the phenyl ring alters the selectivity considerably. Some compounds such as CIPC as well as the analogous secondary butyl ester control broadleaf weeds *and* grasses while IPC for example does not control crabgrass and mustard but is effective on ryegrass. The widespread idea that the carbamates substituted in the phenyl ring with various atoms or groups behave like IPC, which controls predominantly grasses and leaves broadleaf weeds untouched, is only partly true. Some selectivities of carbamates are primarily of positional nature only. According to Shaw this is especially true for grass crops such as corn and wheat, while cotton is physiologically more resistant to the carbamates.

The next interesting group where a study of the structure and activity could be made is the urea group. Asymmetric substituted ureas can be made in a practically unlimited number. From the outside it is difficult to judge how many ureas were synthesized and tested by the DuPont investigators. From the various patents issued the number must be quite considerable. Among this great variety of compounds a chemically closely related group has found so far the most interest. These chemicals are fenuron, monuron, diuron and neburon. They all have in common a phenyl ring which is either unsubstituted or substituted in para respectively in 3,4–position by a chlorine atom. The aliphatic part is either dimethylamine or in the case of neburon methylbutylamine.
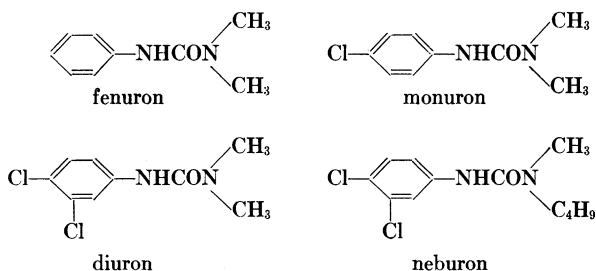


Due to the different solubilities of these chemicals in water and organic solvents, their behaviour in soil is different. While fenuron and monuron are leached to deeper root zones, diuron and neburon stay near the very surface. The difference in absorption on the soil may be another important factor in the reaction versus plants grown in soil. With the solubility the absorption is likely to be as deciding a factor as the absolute phytotoxicity in this group of compounds. As very little is published on the structure/activity relationship in the urea group, my description is far from being complete and is based on a small number of representatives only. The ureas with the best herbicidal activity known to me are the asymmetric aryl–alkyl–ureas. Ring-substituents which are favorable are halogen especially chlorine atoms, but alkoxy–phenyl–alkyl ureas are active also. The aliphatic substituents are preferably low alkyl groups. According to investigations done independently by BASF and Geigy, N. Y., the dimethyl–amino group in monuron and the like can be replaced by a methyl–cyano–methyl–amino group whereby the herbicidal properties remain, but the compounds are less stable and did not find a practical use:
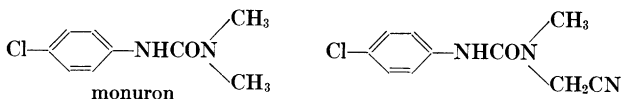


By hydrolysing the cyano-group the respective hydantoins are obtained which are still active.
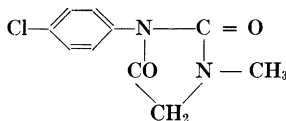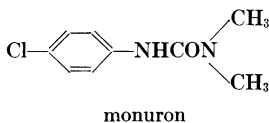
monuron

In order to decrease the residual effect of monuron, BASF researchers claim that hydroxy–alkyl–substituted monuron-like ureas show promise as selective weedkillers:
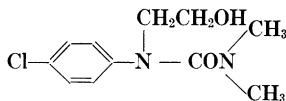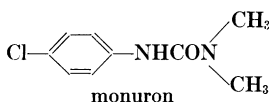


monuron

By substitution of the oxygen atom by a sulfur atom in the monuron-type ureas some herbicidal activity remains, but generally the thio–ureas show an inferior activity in comparison with the analogue ureas.

Let me turn now to the only group I can speak of our own investigations, namely, the triazine herbicides. When we started to synthesize and test triazines in 1952, we decided to screen all our new compounds in Switzerland as well as in the United States to give the chemists the best possible guidance. The methods used consisted in germination and phytohormone tests which differed somewhat in the two laboratories. They were followed by pre- and post-emergence applications of the herbicide candidates. We used this double-check procedure for more than two years when it became evident that the agreement between the test-laboratories had reached such a perfection that we could give up the screening work in New York. Since 1955 only the promising compounds are being sent to this country. Here they are tested under various conditions on a variety of crops by our own people as well as by Federal and States Research workers. Only due to this help from USDA-, University- and Experiment Station-scientists it was possible for us to evaluate the herbicidal properties of a large number of chemicals in a relatively short time. I should like to express at this place my very sincere thanks to all biological workers in this country who took an active interest in our compounds. I hope that they will keep their enthusiasm for new compounds in the future also. In this way the farmer can expect to get more and more selective compounds and his goal to replace the hand-weeding completely may be reached some day.

Let us draw our attention in the first place to the triazines which have still 2 chlorine atoms in the ring. It could be shown that the triazines having in addition to the two chlorine atoms groups bound over an oxygen or sulfur atom and over amino groups respectively are of particular interest. If in cyanuric chloride one of the three chlorine atoms is replaced by one of the above mentioned groups we have to differentiate between products which have predominantly

fungicidal or herbicidal properties. Wolff et al. found that 2–arylamino–, especially 2–chloroanilino–4,6–dichloro–s–triazines have considerable fungicidal activity. If instead of an *anilino* an *aliphatic amino* group is in 2–position of a 4,6–dichloro–triazine, the compounds are good contact herbicides:
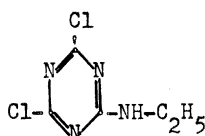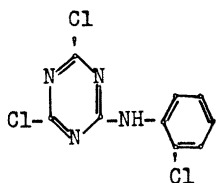


So the substitution of a phenyl ring by an alkyl group results in a fundamental change of the biological properties. If the aliphatic amino-group in a 2–alkyl–amino–4,6–dichloro-triazine is replaced by alkoxy– and alkylthio-groups respectively the compounds remain herbicidally active.
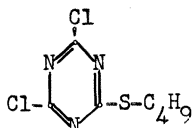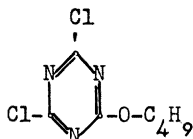


These dichloro–alkylamino–, alkoxy– and –alkylthio–triazines are relatively unstable chemicals. With an increased chain length the stability towards hydrolysis is somewhat increased, but it is doubtful that these compounds on which Koopman and co-workers published will ever find a practical use.

Due to the nearly unlimited number of 2–chloro–4,6–disubstituted triazines which can be synthesized, I should like to discuss this group in various subdivisions
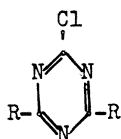


| | | activity | |
|---|---|---|---|
| R = | O–aryl | 0 | a.) |
| | O–alkyl | + | b.) |
| | N–aryl | 0 | c.) |
| | N–aralkyl | + | d.) |
| | N–alkyl | ++++ | e.) |

a) 2–Chloro–4,6–bis–aryloxy–s–triazines and their sulfur-analogues respectively have—as described by Wolff—some fungicidal activity but are of no practical value as selective herbicides.

b) 2–Chloro–4,6–alkoxy– and –alkylthio–s–triazines respectively are significantly more active as herbicides than the aryl–analogues but their activity is a mediocre contact toxicity only.

c) 2–Chloro–4,6–bis–arylamino– or 2–chloro–4,6–bis–N–alkyl–N–aryl–amino–s–triazines which are told by Wolff to have some fungicidal activity also are practically inactive up to 50 pounds/acre as herbicides.

d) 2–Chloro–4,6–bis–aralkylamino–s–triazines, however, show definite phytotoxic activity.

e) As soon as the aromatic amines are replaced by aliphatic amino groups thus forming 2–chloro–4,6–bis–alkylated amino–s–triazines the picture is fundamentally changed as within this group of chemicals there exists a large number of very effective herbicides.

Historically the first active chemical of this group which we synthesized was the 2–chloro–4,6–bis–diethylamino–s–triazine known under the generic name *chlorazine:*

$$\text{Cl}$$

$$(C_2H_5)_2N- \quad -N(C_2H_5)_2$$
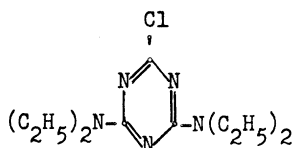
This compound is very stable in neutral and alkaline solutions while in strong mineral acid solutions even at room temperature hydrolysis takes place. The water solubility of chlorazine is in the order of 10 ppm only. On the herbicidal activity of this compound we published a short note in Experientia in 1955. Already in the first screening tests it became evident that this chemical did not possess any phytohormonal activity and that in the germination test a little effect was evident 10 days after application only. The young growing plants, however, died between 10 and 20 days after treatment when the compound was thoroughly mixed with the soil at the beginning of the experiment. In a pre-em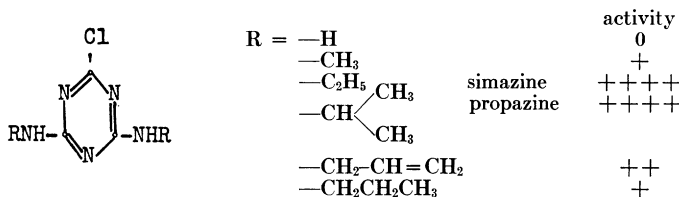ergence test 10 pounds chlorazine per acre killed mustard and oats after 20 days. In pre-emergence field screening tests on a variety of crops it became evident that this compound kills or seriously injures in dosages of 10 lb/A most weeds and crops with the exception of corn where no phytotoxic symptoms could be noticed at all. These observations were the starting point for the synthesis of a long series of triazine-compounds. A considerable number of these chemicals were tested in addition to the laboratory- and greenhouse-tests in the field. I cannot name all the persons who were involved in this project but I wish here to thank all my co-workers, the chemists Rumpf and especially Knüsli, the biologists Gast and Grob, who did most of the screening and field screening work respectively, and Roth, who made a thesis on the metabolism of triazines in plants. I wish to extend my thanks to the analytical chemists for the development of micro-and macro-analytical methods, to the biochemists who helped to elucidate the mode of action of the triazine herbicides and to the toxicologists and pharmacologists for their valuable data on the behaviour of triazines on various laboratory animals.

For the following discussion of the 2–chloro–4,6–bis–alkylated–amino–s–triazines I wish to choose arbitrarily two subgroups:

a) the symmetrically substituted 2–chloro–4,6–bis–alkylated–amino–s–triazines

b) the asymmetrically substituted 2–chloro–4,6–bis–alkylated–amino–s–triazines

a) *Symmetrical 2–chloro–4,6–bis–amino–s–triazines*

The simplest derivative of the series, the 2–chloro–4,6–bis–amino–s–triazine, is of no activity at 10 lb/A. The lowest symmetrical 2–chloro–4,6–bis–alkylamino–s–triazine, the 2–chloro–4,6–bis–methylamino–s–triazine is slightly active only.



| | | | activity |
|---|---|---|---|
| R = | —H | | 0 |
| | —CH₃ | | + |
| | —C₂H₅ | simazine | ++++ |
| | —CH(CH₃)(CH₃) | propazine | ++++ |
| | —CH₂–CH=CH₂ | | ++ |
| | —CH₂CH₂CH₃ | | + |

But already the next homologue of this series is the best 2–chloro–triazine having two identical substituents in 4- and 6-position known so far; it is the 2–chloro–4,6–bis–ethyl–amino–s–triazine: *simazine.* By increasing the chain length of the amino-groups to three carbon atoms three derivatives are possible:

2–Chloro–4,6–bis–isopropylamino–s–triazine
2–Chloro–4,6–bis–allyl–amino–s–triazine
2–Chloro–4,6–bis–*n*–propylamino–s–triazine

of which the first, *propazine,* is the most interesting one:
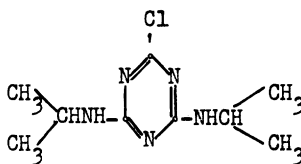


One carbon atom more in the aliphatic amino groups leads to weaker herbicides already and in comparison with simazine and propazine they are of no practical interest. It is unbelievable what differences in the biological behaviour occur with these "minor changes" in chemical structure. The physical properties of all the mentioned 2–chloro–4,6–alkylamino–s–triazines are more or less the same; they are extremely little soluble in water: simazine 5 ppm, propazine 9 ppm etc., they are high melting, tasteless and colourless materials, of mammalian toxicities in the range of 5 g/kg. But some cause phytotoxic reactions on a wide variety of plants and are not effective on a relatively small number of crops or weeds in dosages of 1–5 pounds per acre. Some are active in higher dosages only. Those derivatives which are not active at 10 pounds per acre are arbitrarily claimed inactive.

It is outside of the scope of this lecture to try to discuss all the selective herbicidal properties of the active triazines. I should like, however, to draw your attention on relatively small groups of compounds, closely related chemically but showing characteristic differences biologically. The components I wish to compare with each other of the first pair are:

Simazine : Propazine.

Both compounds have a low solubility in common, they are slow acting, but they have—applied in dosages of 10 and more pounds per acre—a residual effect of a year or even more. Both compounds are practically active through the roots only and crops tolerant to these chemicals are corn, asparagus, sugar cane, grapes, all kinds of trees etc. There exist, however, remarkable differences between simazine and propazine. Sorghum, carrots, celery, fennel are rather tolerant to propazine while these crops are mostly killed by simazine in dosages necessary for selective weed control. On the other hand there exist distinct differences between the two compounds on weeds also: wild carrot (*Daucus carota* L.) is not controlled by propazine while simazine in the same dosage gives a complete kill of this weed. Bindweed (*Convolvulus arvensis* L.) is one of the weeds which are rather resistant to simazine and even dosages of 10 lb/A only stunt the growth of this weed while 10 lb/A of propazine in grapes are able to control *Convolvulus* completely under the same conditions. This complete control may be reached, however, only after many months.

b) *Asymmetrical 2–Chloro–4,6–bis–amino–s–triazines*

In the asymmetrically substituted 2–chloro–4,6–alkylated–s–triazines we found a number of interesting compounds. By far the best chemical of this group is the 2–chloro–4–ethylamino–6–isopropylamino–s–triazine: *atrazine:*
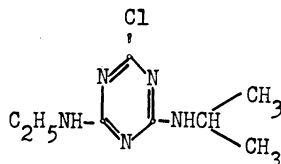


This herbicide is acting more rapidly than simazine and is active against a variety of weeds and crops to which simazine is inactive. Within this group there exist also differences in the selectivity as described before between the symmetrical compounds simazine and propazine. According to Shaw, G 30,451
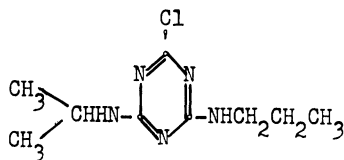


kills walnuts, peanuts and chestnuts to 100% at dosages of 4 lb/A while these crops tolerate G 30,026
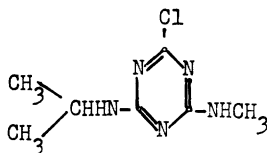
at the same dosages, the weed control of the grasses and the broad-leaf weeds being practically identical. Lima beans and soybeans are completely killed by G 30,026 at 2 lb/A while G 30,451 causes slight injuries at the same dosage to these crops only. Another interesting group consists of asymmetric chloro–triazines being substituted by one primary and one secondary amino-groups. The two most valuable representatives of this type are trietazine and ipazine
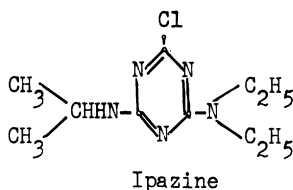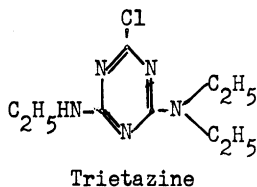


Trietazine                Ipazine

In the screening tests these two compounds behave on a large number of test plants very similarly. Under field conditions trietazine shows selectivity to tobacco, soybeans and peas while ipazine looks promising in cotton. Here also the replacement of one ethylamino-group by an isopropylamino-group causes significant differences in the selective herbicidal properties.

Perhaps the most striking differences are noticeable in comparing a representative of the symmetrical and the asymmetrical chloro–triazines. A typical pair of this kind is
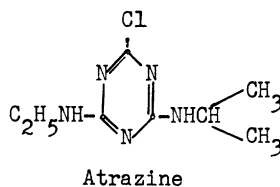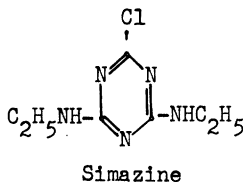


Simazine                Atrazine

Simazine does not penetrate through the leaves and applied as a post-emergence herbicide the activity is through the roots. This is completely different for atrazine which is active even if any root uptake is prevented by covering the soil. Atrazine is about 15 times as soluble in water as simazine and the difference in the solubilities in organic solvents is even more pronounced. It can be expected that deep rooted crops and weeds are more susceptible to atrazine as it is likely to be leached deeper into the soil. It was not foreseeable, however, that this difference in solubility was sufficient to allow the penetration through the leaves for one chemical and to prevent it for the other. In addition to this phenomenon the two chemicals behave in some cases differently where the differences in the solubilities cannot be the explanation for their different biological behaviour. *Panicum* varieties, especially *Panicum sanguinalis*, are controlled fairly well by simazine while atrazine is much inferior against this weed. The same difference exists for *Sorghum halepense* which is not controlled even at fairly high dosages with atrazine. We assume, therefore, that these differences are due to physiological reasons and are not based on the different solubilities of atrazine and simazine respectively.

If in simazine or related chloro–triazines the chlorine atom is replaced by an alkoxy–, especially by a methoxy group, other interesting herbicides are obtained, e.g. *prometone:*
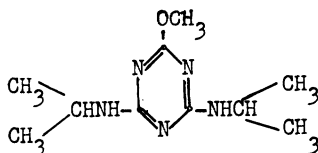


From the physical standpoint the increased water solubility is the first noticeable phenomenon. While the most soluble among the active 2–chloro–4,6–bis–alkylated–amino–*s*–triazines has a water solubility of 250 ppm, the methoxy analogues have water solubilities between 750 and 3500 ppm. This increased solubility enables the 2–methoxy–triazines to enter into deeper root zones. There is, however, a marked difference in the biological behaviour of the methoxy-derivatives as they do not show by far the same degree of selectivity to corn and similar plants. We do not have sufficient data yet to draw conclusions if in this case the rate of uptake of the methoxy–triazines by corn is considerably higher than for the chloro–triazines so that an eventual detoxification does not take place in a rate sufficient to prevent an accumulation of a phytotoxic level in the plant *or* if in this case the corn plant does not possess the system necessary to detoxify the methoxy–triazines. Most of the 2–methoxy–4,6–bis–alkylated–amino–*s*–triazines can be used as post-emergence herbicides. The difference in the biological behaviour of a chloro–triazine in comparison to a methoxy–analogue may be illustrated with the pair:
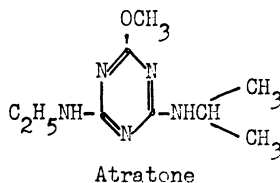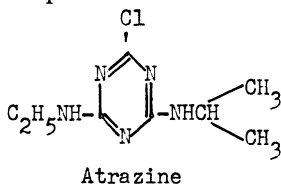


Atrazine                                    Atratone

Amounts up to 10 lb/A atrazine applied pre- or post-emergence are harmless to corn while the same or even considerably smaller amounts of atratone kill or seriously damage this crop. Crops like grapes are much less sensitive to atrazine than to atratone while for beans the contrary is true. Several millet varieties are rather tolerant to atrazine, but are controlled by the same dosages of atratone.

In dosages of 10 to 40 pounds the methoxy triazines proved to be very valuable non-selective herbicides, especially for deep rooted perennial grasses. They can be used either alone or in combinations with simazine or atrazine. Prometone used with a phytotoxic oil at the right growing period is a good brush killer. The volatility of some methoxy–triazines is much higher than for the chloro–triazines: when heated over a period of 31 days at 70° C, 21% of prometone evaporates while simazine and the like disappear to less than 2%.

If the chlorine atom in simazine is replaced by an alkyl–mercapto–especially by a methylmercapto–group another interesting series can be obtained:
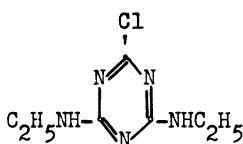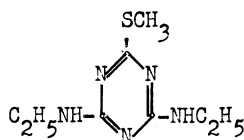


Simazine                                     Simetryne

In the group of 2–methylmercapto–4,6–bis–alkylated–amino–tri-azines we found in the recent past a number of triazines which look very promising. The active representatives of this series have a markedly reduced residual activity in comparison to the methoxy–triazines and especially to the chloro–triazines, thus enabling a use where long residual effects have to be excluded. Generally this group has a somewhat different selectivity in comparison to the other active triazines. Especially some small grains such as barley and wheat, which normally are quite sensitive to triazines, show a somewhat increased resistance to some representatives of the mercapto–triazine group. Corn is about as sensitive to the mercapto–triazine–series as to the methoxy–triazine compounds. Crops such as peas, beans, rape, vetch etc. are fairly resistant to the methyl–mercapto–4,6–bis–alkyl-ated–amino–s–triazines. We hope that these compounds will be available in the forthcoming season to interested research workers.

For the comparison of the chloro–bis–alkylated–amino–s–triazines and the methyl–mercapto analogues I chose the pair simazine/*Sime-tryne* which latter is the generic name for 2–methylmercapto–4,6–bis–ethylamino–s–triazine. The solubility of Simetryne in water is 450 ppm or about 100 times higher than that of simazine. The appearance of the first phytotoxic symptoms occurs faster than in the case of simazine or of most methoxy–triazines. The residual activity of 1–2 pounds of Simetryne is less than 2 months and even the most sensitive crops can be planted after ploughing the soil previously treated with Simetryne or another mercapto–triazine after 3 months. Simetryne has a very high activity applied as post-emergence herbicide and little selectivity. The short lifetime of Simetryne may be of considerable interest for fall or early winter treatments.

If the chlorine atom in simazine and the like is replaced by a hydrogen atom 4,6–bis–alkylated–amino–s–triazines are obtained:
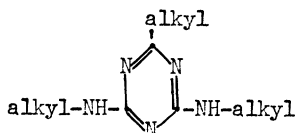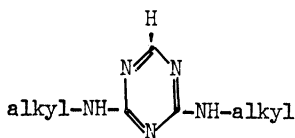


Their activity is considerably lower. But an enhanced phytotoxicity appears as soon as instead of the hydrogen atom a lower alkyl-group is the substituent in 2-position of the 4,6–bis–alkylated–amino–s–triazines. Compounds of this structure have to be synthesized by a

Grignard-reaction or from suitable guanamine derivatives and their production costs are, therefore, considerably higher. In preliminary field tests no specific selectivity could be determined so that this group seems to remain of rather academic interest only.

When the chlorine atom in 2-position of simazine or the like is replaced by a third amino-group thus forming 2,4,6–tris–alkylated–amino–s–triazines
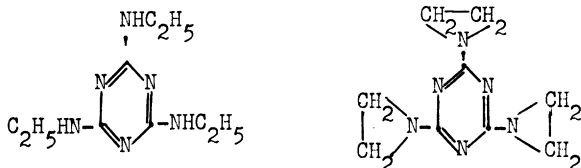


these chemicals have interesting phytotoxic properties also. In comparison to the 2–chloro–4,6–bis–alkylated–amino–s–triazines, however, they are generally of lower activity. Due to their slight basic properties they may be bound to the soil so that they may be inactivated to a higher extent than the chloro-analogues. Practical tests in 1959 with a number of representatives of this class were not promising enough that further investigations are indicated. A compound belonging to the tris–amino–substituted–triazines is the 2,4,6–tris–ethylen–imino–s–triazine. This chemical found considerable interest in cancer research. Due to its structure analogy it was tested in our herbicidal screening tests but did not prove to be active. So apparently due to their cross-linking properties the ethylimino groups are responsible for the cytostatic activity as the herbicidally active triazines of the simazine type do not inhibit the mitosis of the animal cell.

In addition to the various groups I have discussed so far, we synthesized a great many more triazines and a number of analogues of other heterocyclic ring-systems. Generally speaking none of the derivatives surpassed the activity of the best triazines. Some are tested at the time being to such an extent that no definite conclusions can be drawn.

As far as I am able to summarize what we know today about the chemical structure in relationship to the herbicidal properties of the triazine group, the following looks to me as to be a fair statement of the present status of our work:

In the series of substituted symmetrical triazines we found a large number of derivatives which show various degrees of herbicidal activity. The most active herbicides of this series are chemically closely related and are mostly derivatives of s-triazine with 2 alkyl-amino groups and in addition either a halogen atom, preferably a chlorine atom, or an alkoxy—preferable a methoxy—or an alkyl-mercapto, preferably a methylmercapto group. In addition to the two compounds simazine and atrazine, which found so far a practical use as industrial weed killers and as selective herbicides in various crops, propazine, prometone and atratone are in the process to be marketed in this country also, while they are commercialized in

various other countries already. A number of further triazines are tested in the USA and abroad. Slight alterations in the chemical structure lead to considerable differences in the biological behaviour of the various triazine–derivatives. In general the substituents leading to the most active triazines are low alkyl radicals bound over amino groups, oxygen or sulfur atoms and halogen atoms directly linked to the triazine ring. Additional work is necessary to fully evaluate the triazine group. My paper today is a summary of the present status of the investigations in this field only. I hope some day to be able to present you a more complete survey.

If you ask me now what is the role of the chemical research in the development of selective weed control practices I wish to sum up my answer in the following way:

Chemical research is the basis for the development of selective herbicides. The efforts of the synthetic organic chemists have to be guided by their botanical colleagues. The chemical research is, therefore, the first link of a long chain. This first link consists of a little inspiration and a lot of transpiration. It requires patience, confidence and an enormous amount of time and money. A research problem has to give satisfaction to all concerned. The team, consisting of organic, analytical and bio-chemists, biologists, field research workers etc., confronted with the task to develop a selective herbicide must be properly guided so that it can function as a research unit. These conditions have to be coupled with a great deal of optimism to continue a task to the final success whatever difficulties may have to be met. All this taken for granted asks a good dose of luck at the right time, then a new useful product will be the result of the combined efforts sooner or later.